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ORIGINAL ARTICLE

# Efficient transport of lead(II) cations in natural water using a liquid membrane system with dicyclohexano-18-crown-6 as carrier



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## KEYWORDS

Dicyclohexano-18-crown-6;  
Bulk liquid membrane;  
Pb(II) cation

**Abstract** Selective transport of lead(II) cation across a bulk liquid membrane(BLM) containing dicyclohexano-18-crown-6 (DC18C6) as carriers has been studied. Various factors that affect the transport efficiency of this heavy metal cation have been optimized in order to obtain maximum transport. It has been observed that in the presence of EDTA as stripping agent and triton X-100 as sufficient surfactant in the receiving phase and at the optimum pH of 5, lead can transport with recovery  $101 \pm 2\%$ . The carrier can selectively and efficiently transport Pb(II) cation from aqueous solutions containing other interfering cations. A possible application of this carrier system and transport process to the preconcentration and recovery of Pb(II) cation from real samples has also been examined.

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## 1. Introduction

Industrial effluents containing highly toxic and non-biodegradable heavy metal cations are generated in hydrometallurgy, electroplating, and electrochemical industries. For the purpose of environmental conservation and resources recycling, the removal and recovery of the heavy metals have become increasingly stringent (Chmielewski et al., 1997; Kan et al., 2008; Valenzuela et al., 2005). Lead is one of the most extensively

encountered heavy metal in the environment, selective removal of  $Pb^{2+}$  cation for environmental remediation and in the treatment of acute and chronic lead poisoning remains an important objective (Izatt et al., 1985; Hancock, 1986; Damu et al., 1986).

The separation methods used include precipitation reactions, solvent extraction, chromatography and membrane separation. Among all of these techniques, the membrane separation technology is of recent interest (Noble and Stern, 1995a). In recent years, liquid membrane systems are used very often, as alternatives to many other separation and enrichment processes (Noble and Stern, 1995b; Araiki and Tsukube, 1990; Boyadzhiev and Lazarova, 1995). The membrane systems offer greater advantage in terms of energy and matter consumption as well as they offer more selectivity, compared to the other separation systems. For separations at the molecular size in carrier-mediated transport, the liquid membrane systems are

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quite effective and selective (Noble and Stern, 1995b). There are several liquid membrane operation techniques and process designs such as bulk, emulsion and supported liquid membranes. Since the bulk liquid membranes have simple designs and offer ease of control, these are frequently implemented for laboratory studies (Bartsch et al., 1999; Izatt et al., 1986; Altin et al., 2007).

Liquid membranes can carry out extraction and stripping processes simultaneously and they show advantages of non-equilibrium mass transfer and up-hill effect, where solute can move from low-to-high concentration solution (Franken, 1997; Gu et al., 1994; Gaikwad, 2004; Pei et al., 2009).

Selective transport of cationic substrates by membrane carriers is of great importance in chemistry, biology, and separation sciences. Compared with conventional separation processes, such as liquid-liquid extraction, membrane techniques are characterized by the technical simplicity and high efficiency in separating or enriching material from gaseous or liquid mixtures. Membrane techniques have been widely used for carrier facilitated metal ion separations (He et al., 1992; El-Reefy et al., 1996; Kedari et al., 1999; Mishra et al., 1999; Kazemi and Shamsipur, 1999; Safavi and Shams, 1999; Akhond and Shamsipur, 1995; Rezvanianzadeh et al., 2000; Yamini et al., 2002).

In the present paper, the results of an investigation on membrane extraction of lead(II) cation using the bulk liquid technique containing DCH18C6 are reported. Different experimental conditions, e.g. the effect of DCH18C6 concentration in the membrane, type and concentration of stripping agents in the receiving phases, time and etc on  $\text{Pb}^{2+}$  cation transport were investigated.

## 2. Experimental

### 2.1. Reagents

DCH18C6, sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), sodium thiocyanate, thiourea, EDTA, dimethylformamide (DMF) and lead(II) nitrate (all from Merck), sodium hydroxide (Riedel), sodium nitrate (BDH) were used without further purification. Chloroform (BDH), 1,2-dichloroethane, dichloromethane and nitrobenzene (all from Merck) with highest purity were used as liquid membranes. All aqueous solutions were prepared using deionized double distilled water.

### 2.2. Procedure

The transport experiments employed standardized concentric cells in which the aqueous source phase ( $10\text{ cm}^3$ ) and receiving phase ( $30\text{ cm}^3$ ) were separated by an organic phase ( $50\text{ cm}^3$ ). All transport experiments were carried out at ambient temperature. The organic layer was stirred by a Teflon-coated magnetic bar. Speed of stirrer was adjusted so that the phases did not mix with each other. Under these conditions, not only the mixing process is perfect, but also the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined.

The source phase (SP) contained lead(II) nitrate ( $5 \times 10^{-4}\text{ M}$ ). The membrane phase (MP) contained the macrocycle ionophore ( $1 \times 10^{-3}\text{ M}$ ) and the receiving phase (RP), consisted of a stripping reagent ( $1 \times 10^{-3}\text{ M}$ ). In the course of the

transport experiment, samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy (Shimadzu-670).

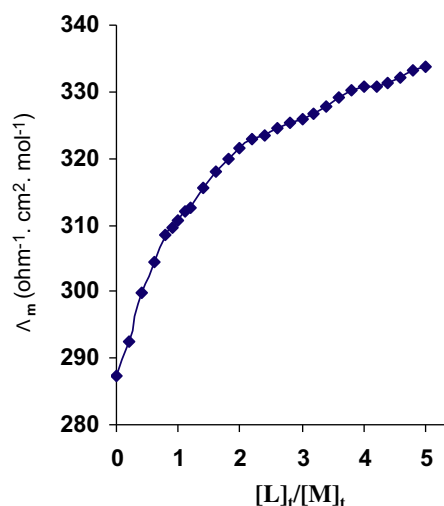
## 3. Results and discussion

### 3.1. $(\text{DCH18C6-Pb})^{2+}$ complexation

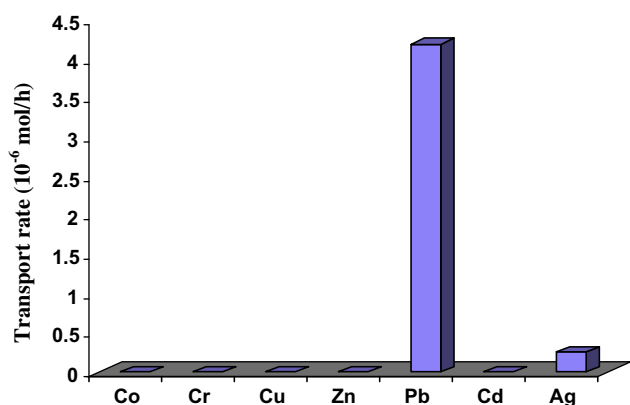
In order to study the complexation process between DCH18C6 and  $\text{Pb}^{2+}$  cation, we used a conductometric titration and the changes of molar conductivity ( $\Lambda_m$ ) versus the ligand to the cation molar ratio ( $[\text{L}]_t/[\text{M}]_t$ ) for this complexation were measured in DMF at  $25^\circ\text{C}$ . As is shown in Fig. 1, a sharp increase in molar conductance is observed, that indicates the complex is more mobile than the cation. The slope of the curve changes at 1:1[M:L], that indicate the stoichiometry of the complex formed between DCH18C6 and this heavy metal cation is 1:1. The formation constant of  $(\text{DCH18C6-Pb})^{2+}$  at  $25^\circ\text{C}$  was calculated from changes of the molar conductance as a function of ligand/cation molar ratios using a GENPLOT computer program (Graphic, 1989) and the  $\log K_f$  value was found to be:  $3.09 \pm 0.04$ . The details of calculation of the stability constants of complexes by conductometric method have been described in reference (Rounaghi et al., 1997). The  $\log K_f$  value indicates that DCH18C6 is a suitable carrier to operate as phase transport catalyst to separate  $\text{Pb}^{2+}$  cation from bulk liquid membrane system. This may be due to the size of the  $\text{Pb}^{2+}$  ( $r = 1.18\text{ \AA}$ ) ion and, therefore, it can attain a convenient fit condition for the dicyclohexyl-18-crown-6 ( $r = 2.2\text{ \AA}$ ) cavity. In addition, in the other experiment, we investigated preliminarily on competitive transport of this cation among some other metal cations (Rounaghi et al., 2011). It was found that DCH18C6 has the desired ability to transport  $\text{Pb}^{2+}$  cation against its concentration gradient through bulk liquid membrane (Fig. 2).

### 3.2. Transport mechanism

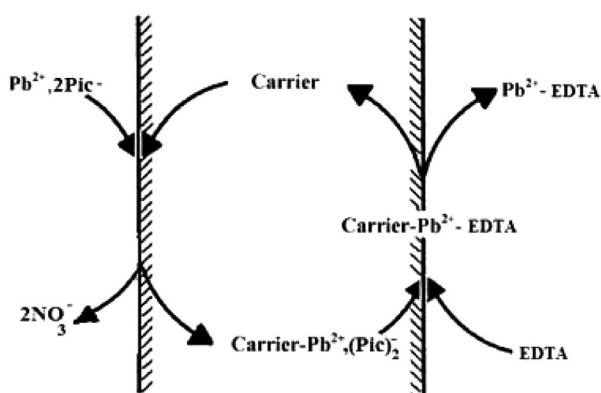
The  $\text{Pb}^{2+}$  cation is transported from the source phase into the receiving phase via a chloroform membrane. The movement of



**Figure 1** Molar conductance-mole ratio plots for  $(\text{DCH18C6-Pb})^{2+}$  complex in DMF.



**Figure 2** The results of competitive metal ion transport (water/chloroform /water) studies for dicyclohexyl-18-crown-6.

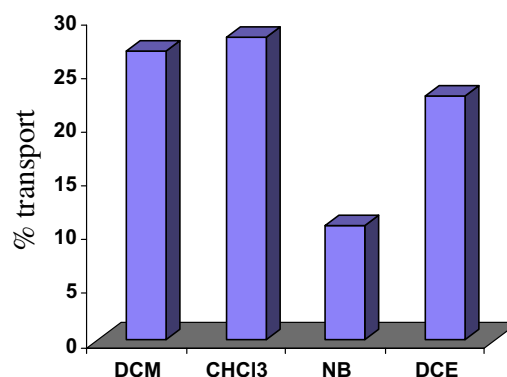


**Figure 3** Schematic of lead transport mechanism.

charged species through the hydrophobic liquid membrane is accomplished by the presence of a cooperative host composed of DCH18C6. After complexation of the carrier with  $Pb^{2+}$  cation on the source boundary phase of the membrane, the complex diffuses down its concentration gradient. On the receiving side of the membrane, the metal ion would be released into the receiving phase via formation of a ternary complex (carrier–metal ion–EDTA). At this stage, the free carrier diffuses back across the liquid membrane. The net result is the transport of  $Pb^{2+}$  cation from the aqueous source phase into the aqueous receiving phase across the bulk of the organic membrane phase. A schematic diagram of this mechanism is shown in Fig. 3.

### 3.3. Effect of type of organic membrane

Selection of a right solvent (or membrane phase) is the prime issue in all kinds of liquid membrane separation processes. The solvent should be chosen in such a way that it is immiscible with the aqueous phase, has low viscosity and volatility and at the same time it should have a high distribution coefficient (Mulder, 1991; Noble and Douglas Way, 1987). In this work, the effect of some organic membrane solvents including: dichloromethane, 1,2-dichloroethane, chloroform and nitrobenzene on the transport efficiency of  $Pb^{2+}$  was studied. The results are shown in Fig. 4. As is evident in this figure, the order of



**Figure 4** Effect of organic membrane on lead transport [source phase (10 ml) with pH 5, contained lead(II) nitrate ( $5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (30 ml) with pH 3, consisted of EDTA ( $1 \times 10^{-3}$  M)].

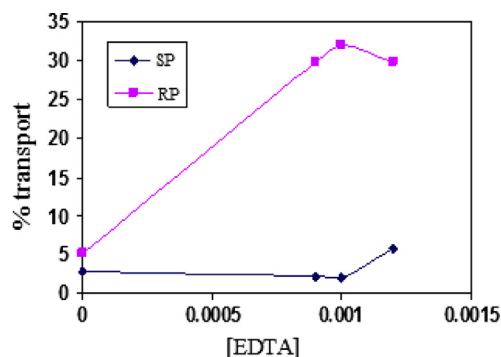
transport rate of  $Pb^{2+}$  cation through organic solvents is: chloroform > dichloromethane > 1,2-dichloroethane > nitrobenzene. The partitioning of ions into the organic phase should be affected by the dielectric constant (Izatt et al., 1986; Bartscha et al., 1999). Dielectric constants of these solvents decrease in: 1,2-dichloroethane > nitrobenzene > dichloromethane > chloroform. Since chloroform has the lowest dielectric constant, therefore, the partitioning of the result complex into it is easier than the other organic solvents. Also this may lead to stabilization of the ion-pair in the organic phase causing to increase the rate of transport of  $(DCH18C6-Pb)^{2+}$  complex through chloroform as liquid membrane. Chloroform also has higher donor and acceptor numbers. The solvating ability of a solvent as expressed by the Gutmann donor number, plays a fundamental role in complexation reactions between metal cations and macrocyclic ligands and a solvent with a high donor number can compete strongly with the ligand for the cation leading to a weaker  $(DCH18C6-Pb)^{2+}$  complex than the other solvents. This character may lead to that chloroform can easily release metal cation to the receiving phase however, other parameters can be effected in chloroform performance.

### 3.4. Effect of type and concentration of stripping agent in the receiving phase

Preliminary experiments revealed that the nature and concentration of the stripping agent in the aqueous receiving phase could have a significant effect on the efficiency of transport of the  $Pb^{2+}$  cation. As it is seen from Table 1, among different stripping agents used in this study, the EDTA with increased complexing ability toward  $Pb^{2+}$  cation acts as the most suitable receiver for the release of this cation from the membrane phase into the receiving phase. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA), can form stable and soluble complexes with heavy cations and thus substantially increase heavy metals removal from contaminations. In addition, although using EDTA in removing pollutions was demonstrated to be widely applicable and economically feasible with acceptable environmental risk, that a number of studies has been carried out on the addition of EDTA and recovery of heavy metals from washing effluents (Wasay et al., 1999;

**Table 1** Effect of type of stripping agent on the  $\text{Pb}^{2+}$  transport [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M) and  $\text{NaNO}_3$  (10 w/v%), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (11 ml) with pH 5, consisted of different stripping agents ( $1 \times 10^{-3}$  M) and triton X-100 ( $1.4 \times 10^{-3}$  M)].

Stripping agent	Percentage transported into receiving phase	Percentage remaining in source phase
$\text{SCN}^-$	9.28	5.6
$\text{P}_2\text{O}_7^{2-}$	10.47	27.2
EDTA	101	0
Thiourea	10.07	12.17

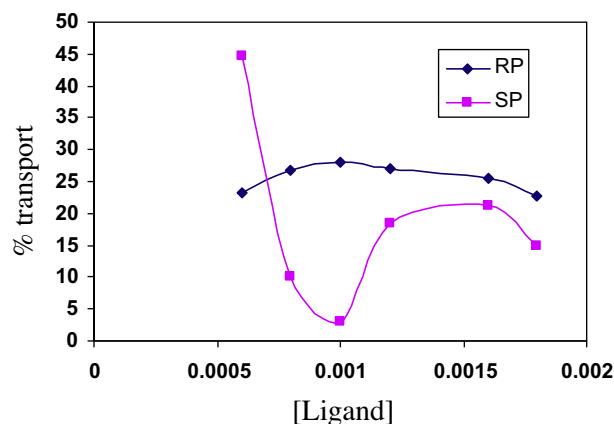


**Figure 5** Effect of EDTA concentration in the receiving phase on lead transport [source phase (10 ml) with pH 5, contained lead(II) nitrate ( $5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (30 ml) with pH 3, consisted of a stripping reagent with different concentrations].

Huang et al., 2000; Juang and Wang, 2000; Palma et al., 2003; Lo and Zhang, 2005). Therefore, we used EDTA for further experiments and the influence of the concentration of EDTA in the receiving phase on the transport efficiency of  $\text{Pb}^{2+}$  was also investigated and the graphical results are shown in Fig. 5. As is obvious, while only 5.23%  $\text{Pb}^{2+}$  cation transport occurs in the absence of the stripping agent, the transport of  $\text{Pb}^{2+}$  cation increases sharply with increasing the concentration of EDTA. The most transport of this cation occurs at  $1.0 \times 10^{-3}$  M of this stripping agent. Thus,  $1.0 \times 10^{-3}$  M EDTA concentration was adopted for further studies.

### 3.5. Effect of concentration of ion carrier in the organic phase

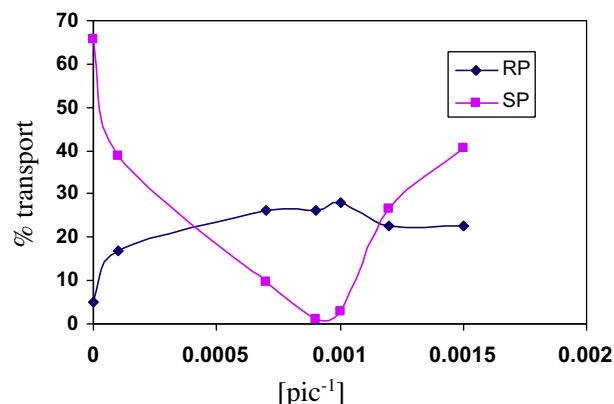
It is well known that in carrier mediated transport, carrier is used to enhance the membrane transport of the solute. The effect of the concentration of ion carrier in the membrane phase on transport efficiency of lead(II) cation was also investigated. The percentage of this cation transported increases with an increase in ion carrier concentration in the chloroform phase (Fig. 6). Maximum transport occurs at a concentration of about  $10^{-3}$  M ion carrier. Further increase in carrier concentration caused a slight decrease in transport efficiency which may be due to more interactions between the metal cation and crown ether in organic membrane, and therefore, causing less delivering the cation to the receiving phase.



**Figure 6** Effect of carrier concentration in the membrane phase on lead transport [source phase (10 ml) with pH 5, contained lead(II) nitrate ( $5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore with different concentrations and receiving phase (30 ml) with pH 3, consisted of EDTA ( $1 \times 10^{-3}$  M)].

### 3.6. Effect of concentration of counter ion in the source phase

In our system, due to simplicity and increasing the  $\text{Pb}^{2+}$  cation transport to the organic membrane phase, we used picric acid as counter ion in the source phase. As is obvious in Fig. 7, while only 4.91% lead ion transport occurs in the presence of the nitrate ion, and about 66% of the cation remains in the source phase and cannot be transported to the organic membrane phase, therefore, nitrate ion is not a suitable counter ion to accompany the  $(\text{DCH18C6-Pb})^{2+}$  complex into the membrane phase. It is well known that the soft, polarizable and weakly hydrated picrate ion is a convenient counter ion that provides greater distribution ratios and membrane transport rates for metal ion–neutral ligand complexes than do inorganic ions such as  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  (Talanova et al., 1999). For this



**Figure 7** Effect of picrate ion concentration in the source phase on lead transport [source phase with pH 5, contained lead(II) nitrate ( $5 \times 10^{-4}$  M) and picric acid with different concentrations, membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (30 ml) with pH 3, consisted of EDTA ( $1 \times 10^{-3}$  M)].

reason, picrate ion was selected as a suitable counter ion. The results are shown in Fig. 6. The flux and efficiency of lead ion transport increase sharply with increasing the concentration of picric acid. The most transport of  $\text{Pb}^{2+}$  cation occurs at a  $10^{-3}$  M of the counter ion. However, a further increase in the concentration of picric acid caused a decrease in the percentage transport of lead ion, most possibly due to the fact that picric acid itself competes with lead(II) nitrate for transport through the BLM system. Thus,  $10^{-3}$  M picric acid concentration was adopted for further studies.

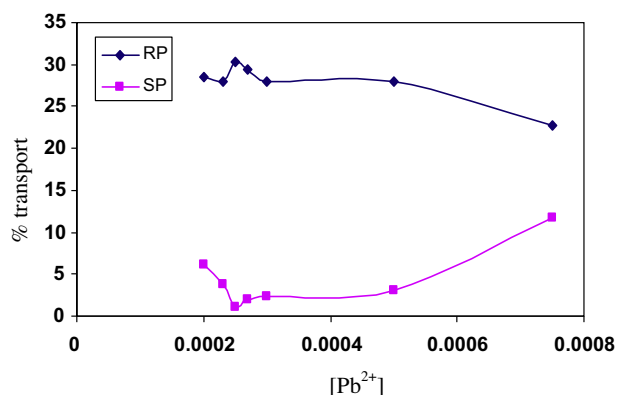
### 3.7. Effect of concentration of lead(II) cation in the source phase

In order to estimate on the ability and performance of our system to separation and purification of  $\text{Pb}^{2+}$  cation, various concentrations of this cation were investigated (Fig. 8). As is evident in Fig. 8, no significant change in recovery was observed with different concentrations of  $\text{Pb}^{2+}$  cation in the samples.

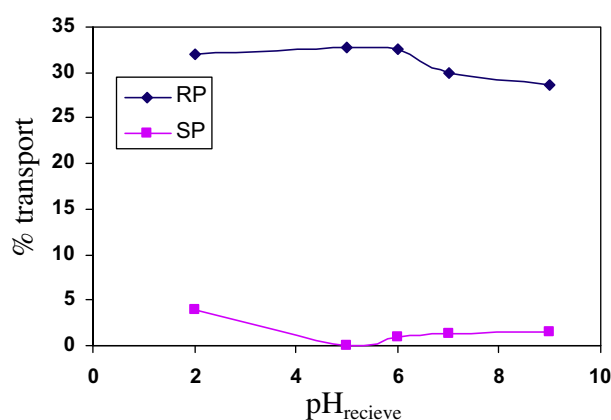
### 3.8. Effect of the pH of the source phase and receiving phase on $\text{Pb}^{2+}$ cation transport

The influence of pH of the source phase on the transport of lead(II) cation can be seen from the graphical results given in Fig. 9. It was found that maximum  $\text{Pb}^{2+}$  cation occurs at pH 3.7. In low pH value, due to low dissociation of picric acid, the concentration of picrate anion reduces which results in decreasing efficiency the lead cation transport. In high pH values the formation of lead hydroxide precipitate will reduce transport efficiency of  $\text{Pb}^{2+}$  cation into the organic phase.

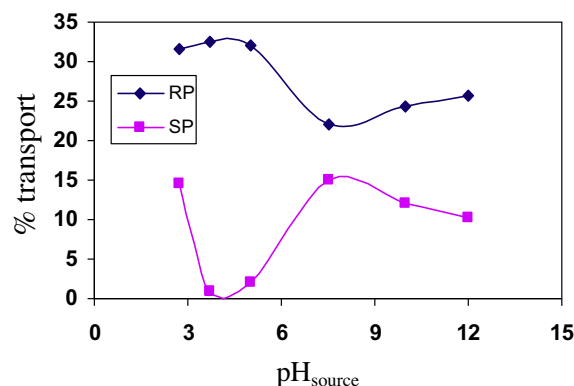
Fig. 10 shows the effect of pH of the receiving phase on the efficiency of lead ion transport. The results reveal that the maximum lead ion transport occurs at pH 5. In this pH, EDTA is in its suitable form and can form a stable complex with  $\text{Pb}^{2+}$  cation in the receiving phase, therefore, pH 5 was selected for further studies. These results show that pH gradient has no effect on lead(II) transport.



**Figure 8** Lead(II) transport in different concentrations of lead nitrate [source phase (10 ml) with pH 5, contained lead(II) nitrate with different concentrations and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (30 ml) with pH 3, consisted of EDTA ( $1 \times 10^{-3}$  M)].



**Figure 9** Effect of pH of the receiving phase on lead transport [source phase (10 ml) with different pHs, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (30 ml) with pH 3, consisted of EDTA ( $1 \times 10^{-3}$  M)].



**Figure 10** Effect of pH of source phase on lead transport [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (30 ml) with different pHs, consisted of EDTA ( $1 \times 10^{-3}$  M)].

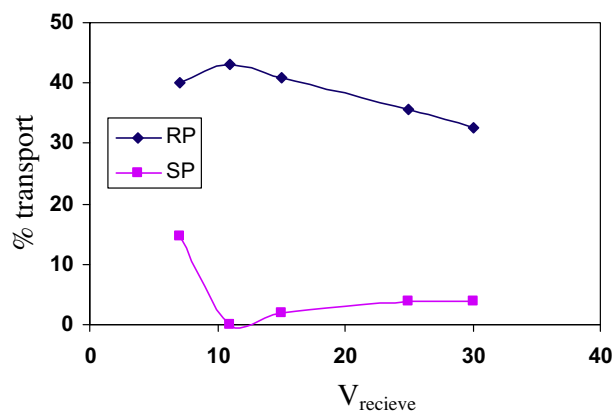
### 3.9. Effect of volume of the receiving phase

In order to increase the preconcentration factor, we studied the effect of volume of the receiving phase. The results are shown in Fig. 11. The optimum volume was obtained in 11 ml, therefore this volume was chosen for further investigation.

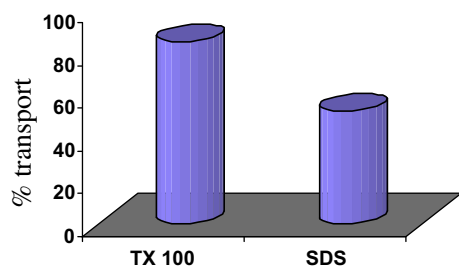
### 3.10. Effect of type and concentration of surfactant in the receiving phase

In this work, we examined the effect of an anionic surfactant (SDS) and nonionic surfactant (Triton X-100) in the receiving phase (Fig. 12). It is currently well established that surfactants form monolayer films at the water–organic interface. Surfactants are essentially low-molecular weight chemical compounds, with molecules that consist of combinations of a water-soluble (hydrophilic) and a water-insoluble (hydrophobic) part. The hydrophobic part is generally a long chain hydrocarbon, whereas the hydrophilic part of the molecule is





**Figure 11** Effect of volume of receiving phase on lead transport [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (different volumes) with pH 5, consisted of EDTA ( $1 \times 10^{-3}$  M)].

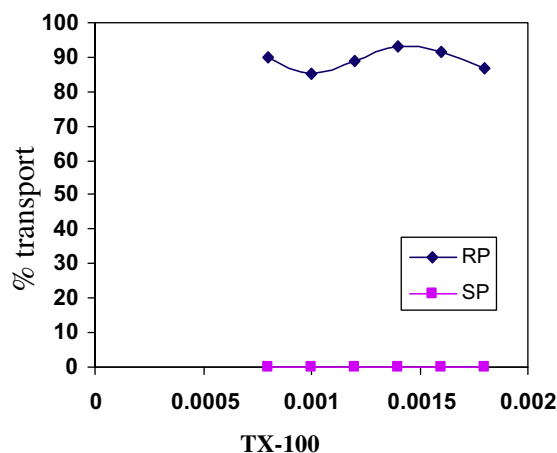


**Figure 12** Effect of type of surfactant [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (11 ml) with pH 5, consisted of EDTA ( $1 \times 10^{-3}$  M) and surfactant].

ionizable, polar, polarizable, and suitable for forming hydrogen bridges. Addition of these surfactants to the receiving phase leads to a better transport efficiency. When we add SDS to the receiving phase, SDS sorbed  $\text{Pb}^{2+}$  via ion exchange, electrostatic attraction. Upon SDS dissociation in water, sodium cation ( $\text{Na}^+$ ) may replace some exchangeable  $\text{Pb}^{2+}$  cation on water-organic surface and dodecyl sulfate anion ( $\text{DS}^-$ ) has negative hydrophilic head that attracts  $\text{Pb}^{2+}$  cations and increases transport efficiency to about 50%. But nonionic Triton X-100 is more effective and can increase transport efficiency to about 90%, because nonionic surfactants show larger depression than anionic surfactants (Manglik et al., 2001), therefore TRITON X-100 due to good surface activity, by the lowering of the surface tension of water and the interfacial tensions between water and organic phase was selected for further studies. The effect of its concentration on transport efficiency was also investigated and the concentration  $1.4 \times 10^{-3}$  M was selected for further investigations (Fig. 13).

### 3.11. Time dependence of $\text{Pb}^{2+}$ cation transport

We studied the time dependence of  $\text{Pb}^{2+}$  ion transport through the liquid membrane under optimal experimental

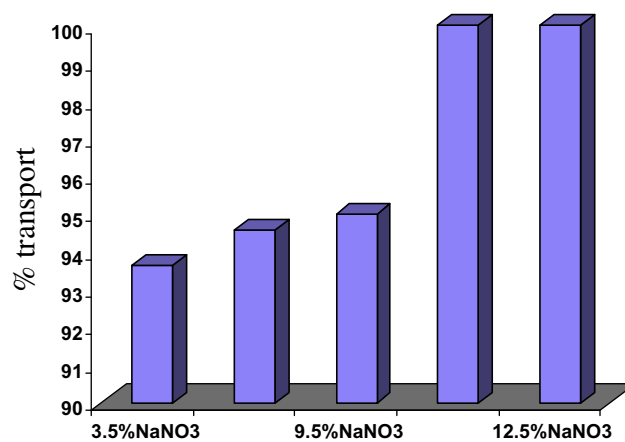


**Figure 13** Effect of concentration of surfactant on receiving phase on lead transport [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (11 ml) with pH 5, consisted of EDTA ( $1 \times 10^{-3}$  M) and triton X-100 with different concentrations].

conditions. It is obvious that both the extraction of  $\text{Pb}^{2+}$  ion from the source phase into the membrane phase and its release from the membrane into the receiving phase are almost after 4 h under the optimum experimental conditions.

### 3.12. Influence of feed phase salinity

Before the application of this separation system for real samples, we investigated the salinity effect of the source phase. Usually, by addition of a salt, the extraction efficiency was enhanced due to salting out effect, whereby water molecules form hydration spheres around the ionic salt molecules. These



**Figure 14** Effect of salinity of source phase on lead transport [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M) and  $\text{NaNO}_3$  with different concentrations (w/v%), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (11 ml) with pH 5, consisted of EDTA ( $1 \times 10^{-3}$  M) and triton X-100 ( $1.4 \times 10^{-3}$  M)].

**Table 2** Effect of interfering ions [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M) and  $\text{NaNO}_3$  (10 w/v%), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (11 ml) with pH 5, consisted of EDTA ( $1 \times 10^{-3}$  M) and triton X-100 ( $1.4 \times 10^{-3}$  M)].

No. of mixtures	%Transport
<i>Mixture 1</i>	
$\text{Pb}^{2+}$	98.49
$\text{K}^+$	4
$\text{Mg}^{2+}$	0
$\text{Ca}^{2+}$	2.6
$\text{Fe}^{3+}$	0
<i>Mixture 2</i>	
$\text{Pb}^{2+}$	96
$\text{Cd}^{2+}$	0
$\text{Zn}^{2+}$	2
$\text{Ag}^+$	0
$\text{CO}_3^{2-}$	0
$\text{Cu}^{2+}$	0

hydration spheres reduce the amount of water available to dissolve analyte molecules in water (Boyd-Boland and Pawliszyn, 1995); thus, it is expected that the target compounds will drive into the organic membrane. For this purpose, in the current work,  $\text{NaNO}_3$  was added into the source phase in the range of 3.5–12% (w/v%). The results show that the extraction efficiency is enhanced due to salting out effect. Addition of  $\text{NaNO}_3$  increases the transport efficiency to maximum amount and according to the graphical results in Fig. 14, the optimal concentration of  $\text{NaNO}_3$  in the donor phase was 10% which was selected for the future studies.

### 3.13. Selectivity of bulk liquid membrane technique

The selectivity of membrane system for the transport of lead cation over other cations, was studied under optimum conditions by carrying out measurements using mixtures of  $\text{Pb}^{2+}$  and different types of cations in equimolar mixtures. The results of this study are given in Table 2.

### 4. Determination of detection limit

The blank determination was performed using optimal conditions. The blank value was  $-0.25 \pm 0.38 \text{ mg l}^{-1}$  of  $\text{Pb}^{2+}$  for 4 replicates experiment, the limit of detection (calculated as 3 times of the standard deviation) being  $1.15 \text{ mg l}^{-1}$  of  $\text{Pb}^{2+}$ . The relative standard deviation of the proposed method was 2%. With  $52.2 \text{ mg l}^{-1}$  of  $\text{Pb}^{2+}$ ,  $\text{Pb}^{2+}$  recovery being  $101 \pm 2\%$ .

### 5. Real water analysis

Three real environmental water samples including ground, river and tap water spiked with lead nitrate were separated and purified using this system under the optimal conditions. Tap water and ground water were collected from Ferdowsi University of Mashhad (Iran), river water was collected from Persian Gulf. The results show that the contents of lead(II) cation in the three samples are all under the detection limit. Therefore, separate

**Table 3** Validation of proposed methodology [source phase (10 ml) with pH 3, contained lead(II) nitrate ( $2.5 \times 10^{-4}$  M) and picric acid ( $1 \times 10^{-3}$  M) and  $\text{NaNO}_3$  (10 w/v%), membrane phase (50 ml) contained macrocycle ionophore ( $1 \times 10^{-3}$  M) and receiving phase (11 ml) with pH 5, consisted of EDTA ( $1 \times 10^{-3}$  M) and triton X-100 ( $1.4 \times 10^{-3}$  M) for  $\text{Pb}^{2+}$  determination in spiked samples].

Sample	Concentration spiked ( $\text{mg L}^{-1}$ )	Concentration measured ( $\text{mg L}^{-1}$ )
River water	58.02	$58.63 \pm 1$
Tap water	52.29	$51.27 \pm 3.5$
Ground water	58.52	$58.53 \pm 1.6$

samples were spiked with a target compound. The results are given in Table 3. It is obvious that  $\text{Pb}^{2+}$  is successfully transported and purified using this new separation system.

### 6. Conclusion

$\text{Pb}^{2+}$  cation can be effectively separated and preconcentrated from water through a bulk liquid membrane containing DCH18C6 in chloroform, allowing the precise and accurate analysis of this metal in real samples. The new method based on liquid membranes offers advantages such as simplicity, lower sample manipulation. It was found that DCH18C6 is a good carrier for selective and efficient transport of lead(II) cation. This study demonstrates the usefulness of the liquid membrane technique for making it possible to combine extraction and stripping operations in a single process and reducing the solvent inventory requirements. The complete transport efficiency ( $101 \pm 2\%$ ) and high degree of selectivity for  $\text{Pb}^{2+}$  cation transport, demonstrated by the studied liquid membrane system, reveal its potential for application to the selective removal and purification of lead(II) cation from real samples.

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